Zero-Emission Coal Technology

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Possil energy is the backbone of the world energy supply and the motor of modern economies. Yet, in spite of its obvious importance, the entire fossil energy sector is threatened by concerns about carbon dioxide (CO₂) accumulating in the atmosphere. The world seems to face a stark choice: curtail economic growth or face potential environmental catastrophe. We are investigating a new technology that will allow us to continue to use our vast fossil energy sources without releasing CO₂ and other emissions to the atmosphere.

Fossil energy sources are vast. Coal reserves alone are sufficient to last for hundreds of years, even with greatly increased world energy consumption rates. Consequently, we have selected zero-emission coal technology as the focus of our program development and research efforts. Zero-emission coal technology could provide low-cost, clean, copious energy from coal for centuries to come without increasing CO₂ levels in the atmosphere.

Our initiative on zero-emission coal technology has led to establishment of the Zero Emission Coal Alliance (ZECA), an alliance of industry, government, and research institutions. ZECA is pursuing a technology for generating hydrogen and/or electricity from coal in an emission-free manner. The process generates a pure stream of CO₂ that can be disposed of in any number of sequestration approaches.

The Los Alamos Approach

Our long-term goal (which is shared by ZECA) is to have a zero-emissions fossil-fuel-based energy source that converts CO₂ into a solid (mineral) by reacting it with an appropriate starting material, possibly in an industrial process. The concept is illustrated in Figure 1. The advantage of our approach is that it addresses the full fuel cycle with the

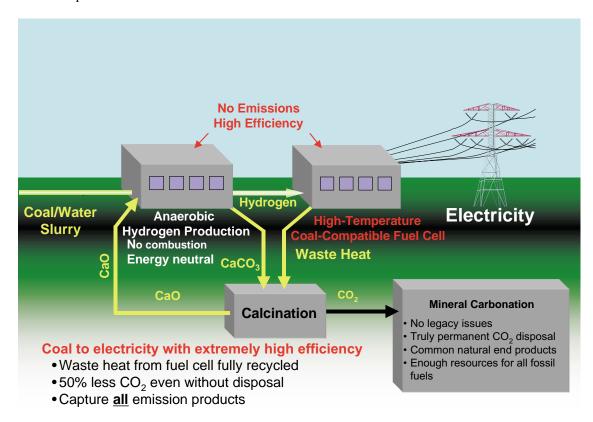


Figure 1. Zero-Emission Coal Process.

The diagram shows conversion of coal to electricity with extremely high efficiency. The waste heat from the fuel cell is fully recycled; there is 50% less CO₂ even without disposal; and *all* emission products are captured.

CO₂ being rendered immobile and benign, which avoids costly monitoring and the potential for environmental disaster. Sufficient raw materials in the form of magnesium silicates exist to handle all of the world's coal easily. The end products (magnesium carbonate and silica) are stable solids, thereby guaranteeing the permanent sequestration of the CO₂.

The full coal gasification and power production process that produces a pure stream of CO₂ involves a number of integrated yet distinct modules, as can be seen in Figure 2. In the first module, coal is reacted with hydrogen to produce methane (CH₄). In the second module, the methane is reacted with lime (CaO) and water to produce calcium carbonate (CaCO₃) and hydrogen (half of which is recycled back to the first module). These first two modules comprise the anaerobic production of hydrogen. In the third module, the (CaCO₃) is calcined to produce a pure stream of CO₂ and lime (which is recycled to the second

module). In the fourth module, the hydrogen is used by a solid oxide fuel cell to produce electricity, water, and heat (used in the third module). The net effect of this process is that coal is used to generate electricity in a highly efficient zero-emission coal plant, which inherently generates a separate waste stream of concentrated CO₂ containing all the carbon brought into the process as coal. This stream of CO₂ is subsequently transferred to a separate mineral carbonation plant to be reacted with magnesium silicates derived from serpentinites or peridotites. The end products are returned to the serpentine mine. Alternative fates for the CO₂ (for example, use in enhanced oil recovery) are also compatible with our zero-emissions gasification concept, but the objective is the safe and permanent storage of CO₂. The process described above is likely to be the only one that will fully meet this objective.

In Figure 2, the material flow is represented in an idealized schematic,

emphasizing the dominant compounds produced in each step. Coal enters the gasification vessel as a slurry or dry material and is then gasified with hydrogen. In contrast to the coal-based, combined water-gas production and shift reactions, hydrogenation of carbon to methane is exothermic. By injecting water into the gasifier, one can quench the heat release and maintain a constant temperature in the gasifier vessel. By transforming the carbonaceous compounds of the fuel into gaseous forms, the gasifier separates the ash from the fuel. The carbon, which is now in the form of volatile carbon compounds, enters the carbonation vessel where it reacts with water to form CO₂ and H₂. The CO₂ is continuously removed from the reaction zone by reacting it with CaO to form CaCO₃. The mixture of liquid water, steam, volatile hydrocarbons, and CaO that reacts in this vessel neither consumes nor generates heat. The energy neutrality follows from the observation that the net reaction

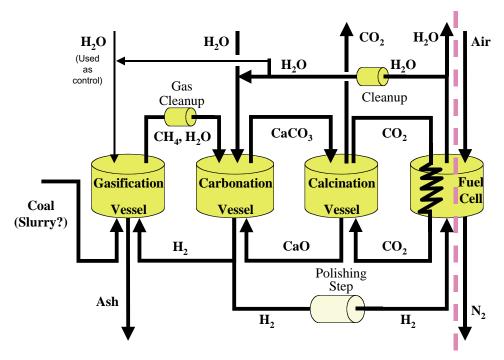


Figure 2. Anaerobic Hydrogen Production and Fuel Cell System.

Material flows in the diagram are idealized to the predominant components. The major reactions are:

Gasification Vessel: $C + 2H_2 \rightarrow CH_4$, H_2O (liquid) $\rightarrow H_2O$ (gas)

Carbonation Vessel: $CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$, $CaO + CO_2 \rightarrow CaCO_3$

in the gasification and carbonation units is essentially energetically neutral:

 $CaO + C + 2H_2O \text{ (liquid)} \rightarrow CaCO_3 + 2H_2 + 0.6 \text{ kJ/mol C.}$

Thus, the total heat release in the gasification and carbonation vessels is zero. Because the first vessel has been adjusted to have zero heat release, the second one will have zero heat release as well. The reaction in the calcination vessel requires heat, which is provided by the solid-oxide fuel cell (the fourth module). For thermodynamic reasons, at their operating temperature, these fuel cells cannot avoid turning approximately one-third of the chemical energy of hydrogen oxidation into waste heat. However, solid-oxide fuel cells operate at a temperature at which this waste heat can be used to calcine CaCO₃. The overall system is highly efficient because it uses the waste heat of the fuel cell to regenerate lime. In the theoretical limit of pure carbon, zero heat losses, and optimal performance of the fuel cell, the efficiency of converting the carbon fuel into electricity would be 93%. Additional losses occur because heat will escape from the vessels and because a realistic conversion efficiency for a fuel cell is less than the thermodynamically allowed limit. Nevertheless, a very high conversion efficiency, on the order of 70 to 80% (compared with 30 to 35% for today's power plants), for the conversion of coal energy to electrical energy should be achievable. It is important to note that for the ZECA process, the 70 to 80% efficiency values already include the efficiency reductions associated with separating out the CO₂ in a pure stream and compressing it to high pressure. The above efficiency values for the conventional plants do not yet include these reductions. Estimates of the efficiency penalty of incorporating the required retrofits into existing power plants would reduce their net efficiencies to approximately 25%.

The process is also attractive because it eliminates all emissions to the air. This process has no smokestack, as there is no combustion of the coal. Thus, the ash (particulates) in the coal is fully contained, making compliance with proposed particulate emission restrictions straightforward. A small amount of additional calcium oxide or CaCO₃ is used to capture the sulfur in the coal. The sulfur is pulled out of the reaction vessels in a solid form, thereby eliminating hydrogen sulfide or SO_x emissions. The reducing conditions inside the hydrogen production vessel and the absence of any combustion limit the formation of NO_x from any nitrogen in the coal. Finally, the CO₂ generated in the hydrogen production is initially extracted as a solid, before being converted to a pure gas stream. Because this extraction is an integral part of the hydrogen production process, no additional expenses are incurred in producing a concentrated

CO₂ exhaust stream.

To dispose of the CO₂ permanently, we are investigating a process to convert it to a stable solid, thereby leaving no CO2 legacy issue for future generations. In our carbonation process, we will react CO2 with abundant, naturally occurring rocks (serpentinites and/or peridotites) to form magnesium carbonate (the magnesium analog of limestone), silica (e.g., quartz), and water. The end products are all naturally occurring, and the reaction is actually part of the natural geological carbon cycle. The reaction that produces the magnesium carbonate (MgCO₃) also generates energy (heat) that could potentially be harvested. The MgCO₃ product is a stable compound, and hence, the disposal is truly permanent. The starting magnesium silicates exist in vast, rich deposits worldwide (Figure 3). For example, a single deposit in Oman contains over 30,000 km³ of the magnesium

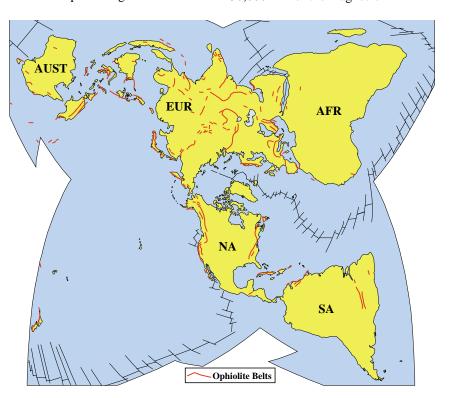
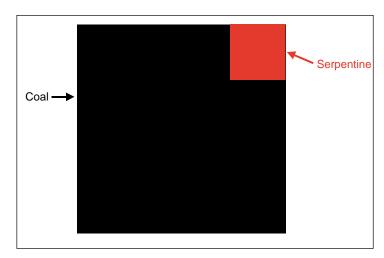


Figure 3. Magnesium Silicate Deposits. The map shows the location of ophiolite belts that are rich deposits of magnesium silicates. Adapted from work by W. P. Irwin and R. G. Coleman, U.S. Geological Survey 1974.



Representative Values for a 1 GW electric power plant at 80% efficiency

	Coal	Serpentine
Thickness	4 m	200 m
Density	1.4 ton/m ³	2.55 ton/m ³
Use/day	3750 ton/day	25,000 ton/day
Area/day	670 m ² /day	49 m ² /day

Figure 4. Disturbed Surface Areas.

The squares represent the surface areas disturbed in supplying the coal and the serpentine for our high-efficiency zero-emission coal process power plant based on the representative values given above for coal and serpentine deposits.

silicates, which alone could handle most of the world's coal. Taken together, the world's rich magnesium silicate deposits are sufficient to handle easily the entire world's coal supply many times over.

The operation scale required is not unreasonable. The serpentinite mining operation suitable for a large electric power plant is smaller than that for a large, open-pit copper mine. Even though the mineral carbonation requires six times the mass of serpentinite compared to the coal used to produce the CO₂, the surface area disturbed in mining the serpentinite is considerably less than that associated with mining the coal. In contrast to coal seams, serpentinites are typically thick and dense, resulting in a smaller footprint for a serpentinite mine than for a coal strip mine. Figure 4 shows an area comparison for coal mining and serpentine mining, assuming typical deposit values.

The end products of the carbonation process would be used to refill the pit. Based on copper ore mining and milling costs and the likely required plant size for the chemical processing, a disposal cost of approximately \$20 per ton of CO₂ would not be unreasonable. With a power plant operating at 80% efficiency, our sequestration approach for CO₂ would cost less than 1 cent per kWh of electricity in the United States.

We believe that coal will likely have an important, and even dominant, position in the energy future for the world. The technological solution we are pursuing with ZECA will allow the realization of "green" coal power, which can be used to ensure a clean world and a long-term, prosperous, healthy, and secure global economy.

Further Reading

For additional information on this topic, please contact Hans Ziock (ziock@lanl.gov).